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GOETHITE DISPERSIBILITY IN SOLUTIONS OF VARIABLE IONIC STRENGTH AND SOLUBLE ORGANIC MATTER CONTENT

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Abstract—The degree of flocculation of aqueous suspensions of microcrystalline goethite was measured in salts of monovalent, divalent and trivalent cations at pH 6.0–6.5 over a range of ionic strengths using light scattering measurements at 650 nm. Varying concentrations of soluble humic material as well as the organic ligands, salicylate and citrate, were tested for their effect on flocculation. It was found that KCl and NaCl induced flocculation at lower ionic strength than $CaCl_2$, while $AlCl_3$ favored dispersion at all ionic strengths tested. The simple organic ligands promoted flocculation at low concentration, with citrate having a more pronounced effect than salicylate. At higher concentrations, these ligands reversed their effect, inducing a more dispersed state of the oxide. The organic ligand effect on dispersibility was modified by the particular metal cation present, with Ca^{2+} being more conducive to flocculation than K^+. Soluble humic materials affected goethite flocculation in a qualitatively similar way to that of the simple organic ligands, that is low concentrations favored flocculation while high concentrations induced dispersion. This dispersing effect was partially suppressed by the presence of Ca^{2+}, and completely suppressed by Al^{3+}. Thus, soluble humic substances at relatively high concentrations appear to have a marked dispersing effect on goethite in the absence of polyvalent cations, and a strongly flocculating effect in their presence.

The results can be explained qualitatively by a simple oxide surface charge model, in which chemisorption of multivalent cations or organic ligands alters the surface charge. Reactions that increase the magnitude of positive or negative surface charge favor dispersion, while those that reduce the magnitude of charge favor flocculation.

Key Words—Citrate, Dispersion, Flocculation, Goethite, Humic Acid, Light Scattering, Salicylate, Soluble Organic Matter.

INTRODUCTION

The factors conducive to clay aggregation and well-structured clay soils are reasonably well-established for soils of temperate regions where permanent-charge silicate clays tend to predominate. Thus, a high Ca base status, near-neutral pH, and substantial organic matter content are associated with optimal soil structure. Although biological activity is critically important to structure in addition to physical chemical factors, the positive effect of Ca^{2+} on the structure of clay-textured soils is attributable in part to the aggregating effect of this exchange cation. Not only does Ca^{2+} cause layer silicate platelets to aggregate into larger quasi-crystalline units (Quirk and Aylmore 1971), it also flocculates humic substances (Ong and Bisque 1968) and bridges between silicate clays and organic matter (Muneer and Oades 1989). Thus, soils with high "base status" typically have quite stable aggregation (Oades 1989).

The stable aggregation often encountered in the highly-weathered clay-textured soils of the tropics has a different origin. Because these soils are typically very acid, Al^{3+} dominates the exchange complex and is a very effective aggregating agent. In fact, amending these soils with $CaCO_3$ to increase Ca^{2+} on exchange sites and reduce Al^{3+} solubility can disrupt the aggregate structure (Fontes et al. 1992a). Organic matter, which bonds strongly with oxides in these soils, for example, goethite (Fontes et al. 1992b), may actually suppress aggregation of the oxide particles. Consequently, oxisols can have more water-dispersible, therefore less aggregated, surface horizons than subsoils (Bartoli et al. 1992). A closer analysis of the basic processes controlling oxide particle dispersion and aggregation is needed to explain this behavior, which is inconsistent with that expected from experience with temperate-region soils.

It is useful to begin with model oxide systems to represent the variable-charge nature of highly weathered soils. When the dispersing and flocculating properties of these simple minerals suspended in water is understood, there is a better chance of explaining the aggregation behavior of variable-charge soil colloids. It is well known that pure oxides of Fe and Al, because they possess no permanent charge, tend to flocculate most completely under neutral to slightly alkaline conditions, that is, at a pH close to their point of zero charge (PZC). This is attributed to the fact that surface charge is minimized at this pH (Stumm 1992). It follows that any adsorption process that modifies the surface charge of the oxide is likely to alter the degree of dispersion. This has been demonstrated for the dispersion of hematite in the presence of some dissolved

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inorganic and organic anions, as well as cations, by Liang and Morgan (1990). Tipping and Higgins (1982) observed that humic substances adsorbed on hematite enhance the stability of colloidal dispersions of this oxide, and there is evidence that the effect arises from charge reversal on the surfaces (Sholkovitz 1976).

In the present study, we investigate the separate and interactive effects of ionic strength, cation type and organic ligand type on the aggregating tendency of goethite, a common mineral of highly-weathered soils. This study is necessary in order to predict the behavior of oxides in contact with soil solutions, where the particles are likely to encounter and adsorb low molecular weight organic acids, humic substances and various inorganic anions. In such a complex chemical environment, the PZC of the "pristine" oxide is unlikely to be relevant in explaining the observed dispersing properties.

MATERIALS AND METHODS

Goethite Preparation and Characterization

Goethite (α-FeOOH) was prepared according to the method of Atkinson et al. (1967). Briefly, this involves the addition of concentrated KOH to ferric nitrate to give a final pH of 12, followed by ageing for 24 h at 60°C. The goethite suspension was dialyzed against distilled water to remove excess KNO_3. Once the water tested negative for nitrate by the brucine test (<0.06 mg/l), dialysis was discontinued. The final oxide suspension, stirred continuously to maintain uniform particle density, contained 8.4 mg of goethite/ml and had a pH of 6.45.

A portion of the goethite suspension was freeze-dried in order to obtain a powder suitable for measuring the surface area and obtaining an infrared (IR) spectrum. The surface area of the goethite was measured at 50.3 m^2/g by application of the Brunauer-Emmett-Teller (BET) equation to nitrogen (N_2) adsorption data obtained at −70°C after 100°C outgassing of the oxide. The IR spectrum of the goethite revealed absorption bands at 3400, 3150, 1645, 1385, 885, 785 and 625 cm^{-1}. The bands at 3400 and 1645 cm^{-1} indicate the presence of water, while bands at 3150 are attributed to goethite OH stretch, 885 to OH in plane and 785 to OH out of plane deformation (van der Marel and Beutelspacher 1976; Wilson 1987). The sharp but relatively weak 1385 cm^{-1} band is attributed to residual entrained or adsorbed nitrate.

To measure the goethite point of zero charge (PZC), 0.5 ml of the original suspension (8.4 mg goethite/ml) was diluted in 25 ml of 10^{-4} M KCl as electrolytic background (total volume = 25.5 ml) then each suspension was adjusted to a different pH value using a negligibly small volume of concentrated KOH or HCl, and the degree of dispersion was measured by light transmittance (see the methods section below on transmittance measurement). The pH values at which the most flocculation was observed were between 7.0 and 7.7, suggesting a PZC in this range. Although this is a lower PZC than reported for goethite based upon potentiometric titration, it is probably shifted to lower pH by the presence of adsorbed HCO_3^- (Lumsdon and Evans 1994), since no attempt was made to exclude CO_2 from the suspensions.

Preparation and Characterization of Soluble Humic Substances

Natural soluble organic substances were extracted from a Carlisle muck soil from New York State, using two parts distilled water to one part soil. This suspension was shaken for two h and then filtered under vacuum. The filtrate had a dissolved organic carbon (DOC) concentration of 749 mg/l, determined by a modification of the Walkley-Black (wet oxidation and reflux with $K_2Cr_2O_7$) method (Greenberg et al. 1992), and a pH of 5.6. After bubbling with nitrogen gas to reduce dissolved oxygen, the extract was stored in the dark in capped polyethylene bottles at 4°C until used for flocculation/dispersion experiments.

Preparation of Solutions of Inorganic Salts and Low Molecular Weight Organic Compounds

Aqueous solutions of calcium, aluminum, sodium and potassium chloride were prepared in concentrations ranging between 100 millimolar (mM) and 1 mM. Calcium acid citrate was prepared by mixing 0.530 g of calcium hydroxide and 1.05 g of citric acid in a 500 ml volumetric flask. This solution had a final citrate concentration of 10 mM, calcium concentration of 14.3 mM and a pH of 5. Calcium salicylate was prepared by mixing 0.691 g of salicylic acid with 0.185 g of calcium hydroxide in a 500 ml volumetric flask, giving a final salicylate concentration of 10 mM, calcium concentration of 5 mM and pH 5.0. Potassium acid citrate with a pH of 5.00 was prepared by dissolving in 500 ml, 1.06 g of citric acid with 0.633 g of potassium hydroxide. The salicylate solution with a pH of 5.53 was prepared by dissolving in 500 ml, 0.692 g of salicylic acid with 0.321 g of potassium hydroxide. The potassium acid citrate solution was 14 mM in potassium and 10 mM in citrate, and the potassium salicylate solution was 12 mM in potassium and 10 mM in salicylate. Dilutions of these stock solutions were made in order to produce different organic ligand and cation concentrations.

Dispersibility Measurements

Three main dispersion/flocculation experiments were run on the goethite suspension. The final concentration of goethite was held constant in all experiments at 0.16 mg/ml. The initial light transmittance value of this suspension was 14%, but once it was allowed to settle undisturbed for 18 h, the transmit-

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tance increased to 33% (see below for method of transmittance measurement).

In the first experiment, the range of concentration from 0.1 to 10 mM for the four salts, $AlCl_3$, $CaCl_2$, KCl and NaCl, was tested for its effect on flocculation. In all the prepared suspensions, the sequence of addition to 30 ml glass tubes was the following: water, salt solution and stock goethite suspension, giving a final volume of 25.5 ml. These suspension were then shaken for 30 seconds in a Vortex-Genie at speed 8, and allowed to settle for 18 h. After this time, the top 3 ml of the suspension in each tube were pipetted into a cuvet, and percent transmittance measured on a Perkin Elmer Lambda 6 spectrophotometer at a wavelength of 650 nm. This gave a measure of suspended particle density, with lower transmittance corresponding to a higher degree of dispersion. The pH value of each suspension was measured at the time of transmittance measurement to ensure that the pH remained within 0.5 units of the initial pH (6.5). Suspensions containing aluminum salts had a final pH lower than the suspensions in the other salts, calcium, sodium and potassium chloride, ranging from 5.4 to 5.1 depending on the Al concentration. By plotting the measured transmittance values against electrolyte concentration in the suspensions, flocculation curves for goethite in $AlCl_3$, $CaCl_2$, KCl and NaCl solutions were determined.

In the second experiment, the effect of synthetic water-soluble organic ligands, that is citrate and salicylate, on the flocculation of goethite in the presence of calcium and potassium salts was investigated. Three citrate concentrations at 1, 0.1 and 0.01 mM were tested, each one with a range of concentration of $CaCl_2$ and KCl from 0.1 to 10 mM. Similarly, three concentrations of salicylate were tested. Because the final pH of the solutions varied by less than 1 unit, no pH correction was made in order to avoid changing the ionic strength. The suspensions, as in the previous experiment, had a final volume of 25.5 ml and a goethite concentration of 0.16 mg/ml. The tubes were shaken for 30 seconds and allowed to settle for 12 h. Measurements of transmittance were made as in the first experiment.

The third experiment was designed to measure the effect of natural water-soluble organic compounds on goethite dispersibility over a range of salt concentrations. In the first part of this experiment, soluble organic matter extracted from an organic soil, ranging in concentrations from 0.06 to 74.9 mg/l DOC were added to 0.16 mg/ml goethite suspensions while maintaining the total volume at 25.5 ml. In the second part, concentrations of soluble organic matter at 0.08, 0.75, 7.5 and 45 mg/l DOC were tested for their effect on goethite flocculation in the presence of salts. Thus, at each organic concentration, the salt concentrations of $AlCl_3$, $CaCl_2$, KCl and NaCl were varied from 0.1 to 10 mM to observe the effect on flocculation. These suspensions were shaken in tubes for 30 seconds and allowed to settle for 12 h prior to transmittance measurements.

Statistical Analysis

The statistical analysis was done with Minitab™ on an IBM personal computer. Each experiment was set as a completely randomized design, and an analysis of variance for a one way classification was run on the data to evaluate significant differences. Multiple comparisons were run in each set of experiments according to Tukey's procedure (Steel and Torie 1980). The experimentwise error rate was specified at $\alpha = 0.05$.

RESULTS

Effect of Salt Concentration on Goethite Flocculation

The effect of different concentrations of aluminum, calcium, potassium and sodium chloride on the flocculation of goethite suspensions is indicated in Figure 1. Because the upper portion of the suspensions were sampled, higher transmittance values correspond to a more flocculated state of the undisturbed suspensions.

The Na and K salts had similar effects on goethite flocculation with complete flocculation induced at concentrations higher than about 1 mM. The Ca salt failed to induce flocculation below 2 mM, caused incomplete flocculation between 2 and 4 mM, and complete flocculation above 4 mM. Since the variability in these transmittance measurements on duplicate samples is relatively large (95% confidence intervals are approximately ± 4 to ± 6 units of % transmittance), overall differences in the K and Na transmittance data are only marginally significant. However, the Ca salt clearly had an effect on goethite dispersibility different from that of the monovalent salts.

From Figure 1, it can be seen that aluminum chloride produced a markedly different effect from the other salts on the dispersibility of goethite suspensions. No flocculation was observed at any of the tested aluminum concentrations. That is, there was no significant difference between the degree of dispersion in untreated oxide suspensions, for example fully dispersed control treatments, and ones with aluminum salt added. However, it is important to note that the Al-treated suspensions had a decreased pH of 5.0 to 5.5, compared to that of the calcium, potassium and sodium-treated suspensions at 5.8–6.5. Because of this pH variable, a test was done in which the pH of the goethite suspensions was lowered with HCl to a value of 5, in an effort to estimate the effect of low pH itself on dispersibility when aluminum was absent. The results indicated that the suspensions at pH 5 had the same degree of dispersion, with transmittance = 35.8%, as the unacidified oxide dispersions which exhibited transmittance = 35.0%. This suggests that low-

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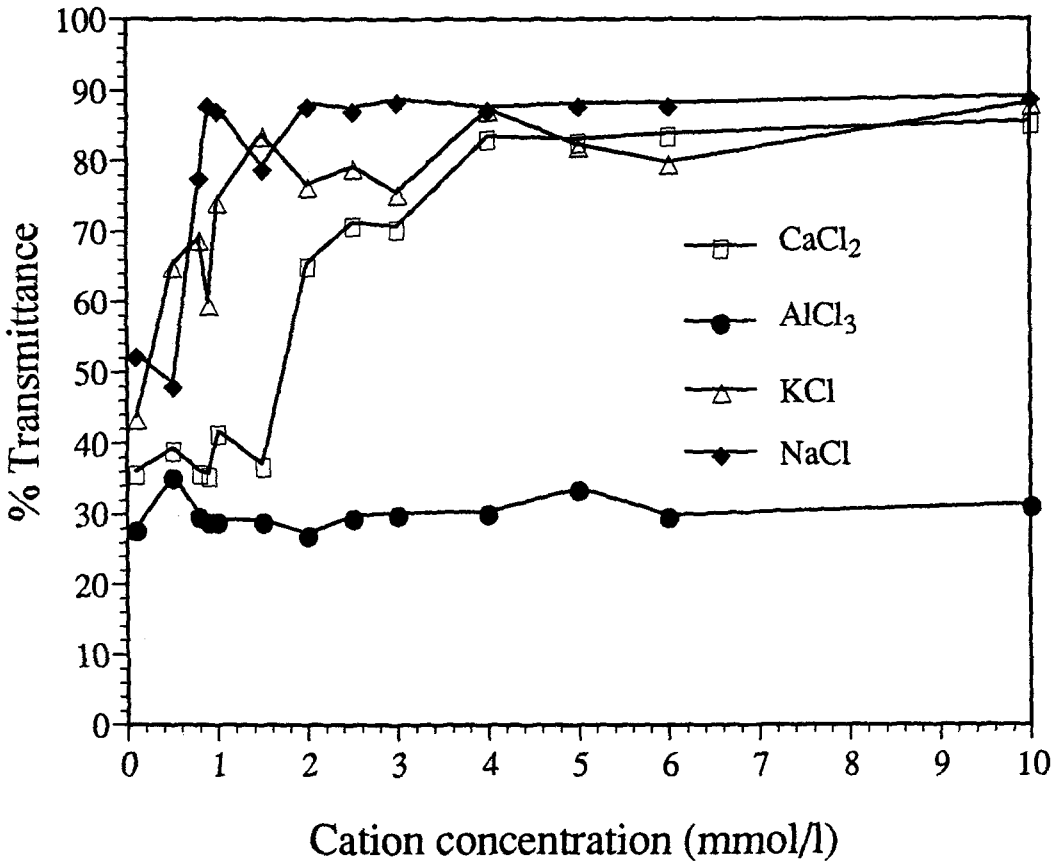


Figure 1. Transmittance of goethite suspensions measured over a range of concentrations of NaCl, KCl, $CaCl_2$ and $AlCl_3$.

er pH did not in itself cause a significantly higher degree of dispersion in the aluminum salt treatments. Furthermore, one would have expected the greater ionic strengths at the highest aluminum chloride additions (Figure 1) to induce flocculation unless aluminum was providing a strongly dispersing effect.

Effect of Water-Soluble Low Molecular Weight Organics on Flocculation

In Figure 2, transmittance is plotted against calcium concentration for three different concentrations of citrate and salicylate (0.01, 0.1 and 1 mM). The curves in Figure 2 show that the presence of citrate at any of the three levels (0.01, 0.1 and 1 mM) promoted flocculation of goethite regardless of the calcium concentration. In comparison, salicylate was less efficient in promoting flocculation at low (<2 mM) calcium concentrations. Nevertheless, salicylate increased flocculation relative to systems in which only goethite and calcium chloride were present. The lower salicylate concentrations of 0.1 and 0.01 mM had a greater flocculation effect than 1 mM salicylate, at least when the calcium concentration was less than 2 mM.

Figure 3 shows the results obtained when the organic ligands, citrate and salicylate, were added to the potassium chloride-goethite suspensions. With the 0.1 and 0.01 mM citrate concentrations, a lower salt concentration was required to flocculate the goethite compared to the same suspension without citrate. In the case of the 1 mM citrate concentration, the reverse effect was observed, a higher salt concentration was needed to flocculate the oxide suspension. The salicylate effect on the potassium chloride-goethite suspensions was different from that of citrate. The presence of salicylate had less effect than citrate on flocculation of the suspensions. Even so, the data in Figure 3 suggests a greater flocculation caused by salicylate at a higher salt concentration (>2 mM), and somewhat reduced flocculation caused by salicylate at lower salt concentration.

Effect of Soluble Humic Substances on Goethite Dispersion

The effect of increasing amounts of soluble organic matter, extracted from a muck soil, on the dispersibility of goethite suspensions is shown in Figure 4. The final concentration of natural organic matter in the suspensions is reported as mg of dissolved organic carbon (DOC) per liter. In the absence of DOC, the transmittance of the dispersed goethite suspension was 38%.

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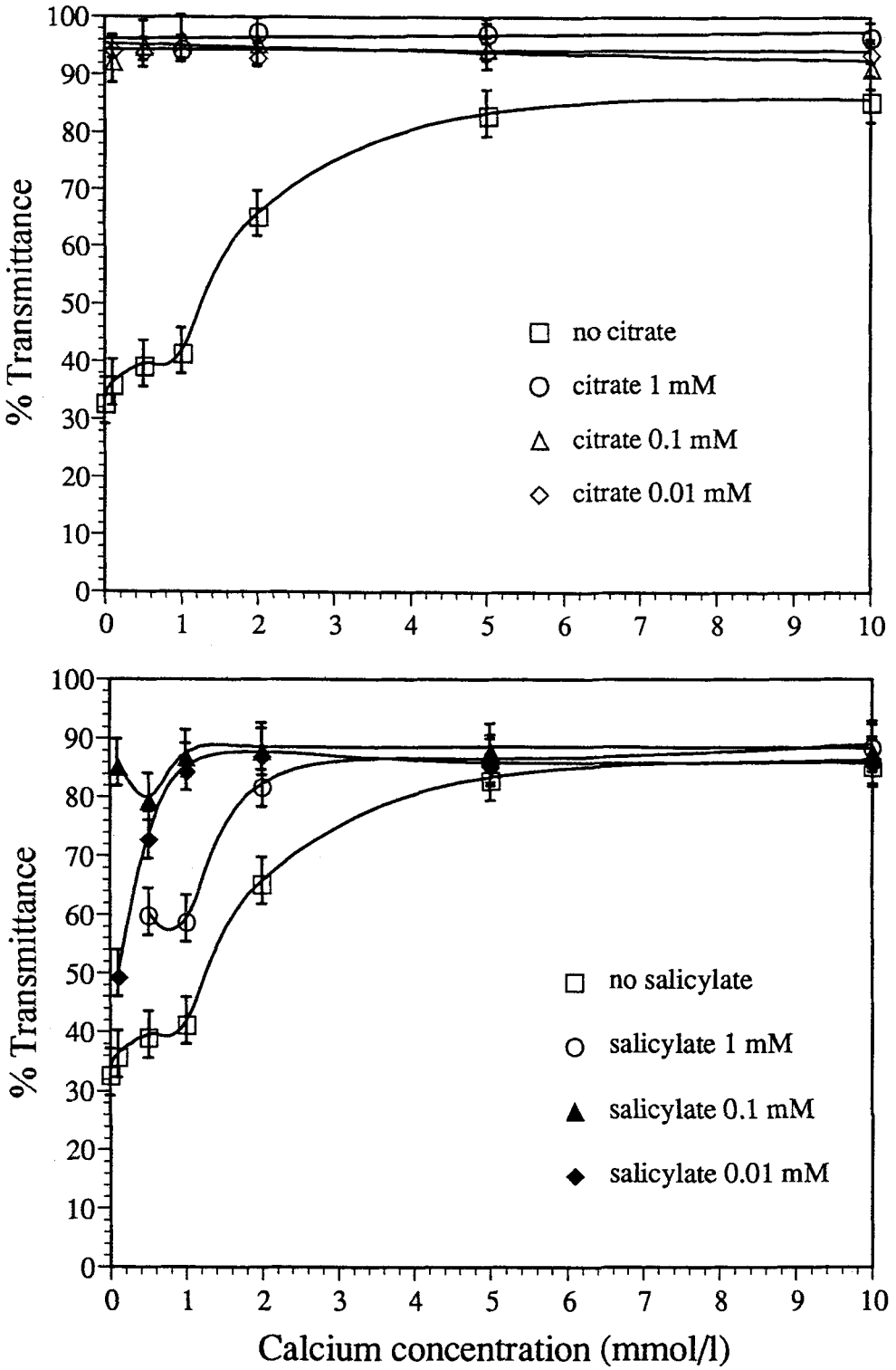


Figure 2. Transmittance of goethite suspensions at three citrate or salicylate concentrations, measured over a range of concentrations of calcium.

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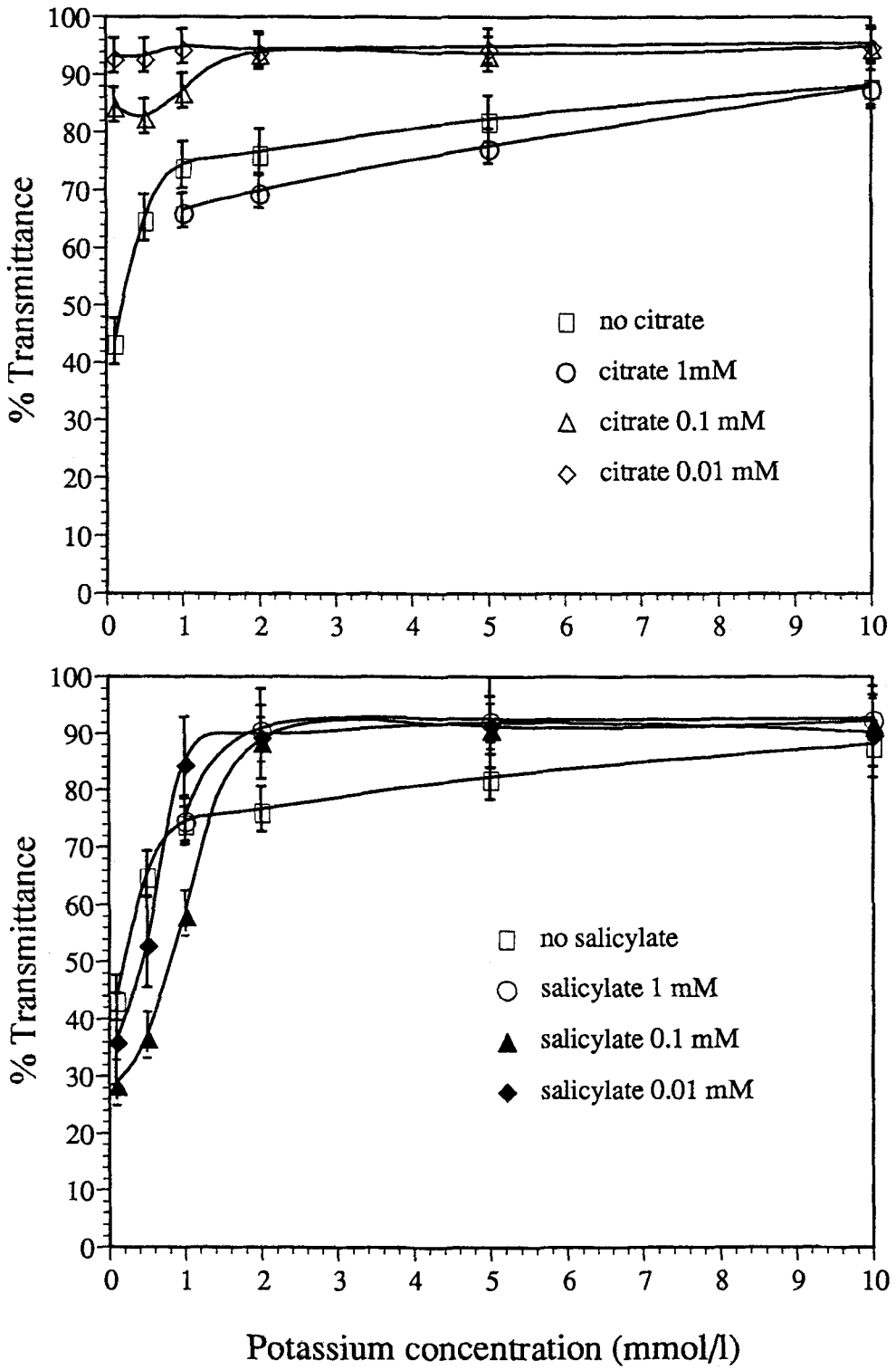


Figure 3. Transmittance of goethite suspensions at three citrate or salicylate concentrations, measured over a range of concentrations of potassium.

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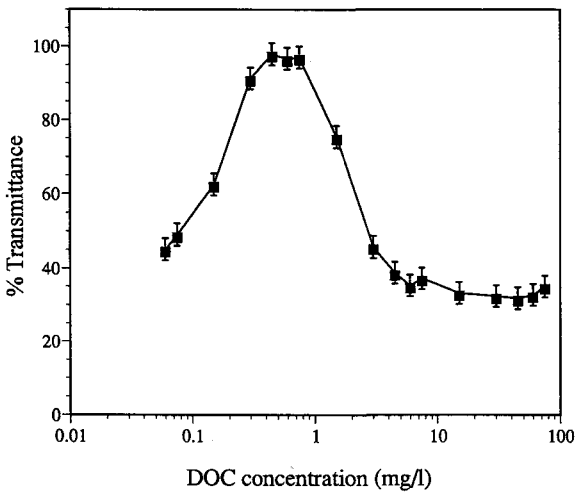


Figure 4. Transmittance of goethite suspensions measured over a range of concentrations of soluble organic matter (DOC) in the absence of added salts.

When the DOC level was increased to 0.15 mg/l, some flocculation was observed, and with DOC concentrations between 0.30 and 1.50 mg/l, all the goethite was flocculated. However, when DOC was increased above 3 mg/l, the oxide remained highly dispersed, as indicated by transmittance of ≈30–35%.

As part of the same sequence of experiments, four concentrations of DOC were used in combination with the four inorganic salts in order to observe the interactive effect of organic matter, ionic strength, and cation charge on flocculation. In Figure 5, transmittance values of goethite with the four levels of soluble organic matter with DOC = 0.08, 0.75, 7.5 and 45 mg/l, are plotted against increasing salt concentration for each salt. In each graph shown in Figure 5, the 0 mg/l DOC curve represents the transmittance of the goethite suspension at increasing concentrations of the particular electrolyte without added organic matter. In the case of Na and K chloride (Figures 5a, 5b), the 0.08 (lowest) DOC level had little effect (Na) or a substantial effect (K) in promoting flocculation. The 0.75 DOC level induced complete flocculation, even at the lowest ionic strength used. However, the highest DOC levels at 7.5 and 45, had a strongly dispersing effect at all ionic strengths. This means that the effect of DOC on goethite dispersibility reversed at some intermediate level.

With Ca chloride present (Figure 5c), flocculation was also promoted by the lower DOC levels at 0.08 and 0.75, with the 0.75 level causing complete flocculation at all ionic strengths. The higher DOC levels promoted dispersion, at least at lower ionic strength, with the highest DOC (45) generating the greatest dispersion.

With Al chloride present (Figure 5d), because the goethite was highly dispersed without DOC addition, the effect of DOC addition was to increase flocculation. Each increase in DOC produced more flocculation, until at 7.5 mg/l or higher, flocculation was complete.

DISCUSSION

The dependence of flocculation of dispersions of layer silicate clays, oxides and organic matter on ionic strength is well known. The Schultz-Hardy rule has long been used to semi-quantitatively relate the minimum salt concentration at which flocculation is induced, termed the critical coagulation concentration (CCC) or flocculation value, to the valence of counterions in solution (van Olphen 1977). Typical flocculation values for layer silicate clays in salts of monovalent cations are in the range of 10–100, divalent cations in the range of 0.1–1.0 and trivalent cations in the range of 0.01–0.1 mM. However, the goethite flocculation results, shown in Figure 1, appear to contradict the Schultz-Hardy rule. Tendency to disperse increased as cation valence of the salt increased. In fact, $AlCl_3$ favored dispersion so strongly that no flocculation value could be detected within the range of $AlCl_3$ concentrations tested. By comparison, $CaCl_2$ produced a flocculation value around 4 mM, while KCl and NaCl had flocculation values close to 1 mM. Much higher flocculation values than these have been reported by Liang and Morgan (1990) for Fe oxides suspended in salts of monovalent cations, but those data were obtained at pH 10.5, conditions highly favorable to dispersion because of substantial negative charge development on the oxide. Thus, our results at near-neutral pH can be taken as more representative of oxide dispersion behavior under common soil conditions.

Apparent non-compliance with the Schultz-Hardy rule is not surprising for goethite at pH 6–6.5, because the oxide is somewhat positively charged at this pH. According to the rule, only the valence of the counterions should affect flocculation and at pH 6, the counterions are anions. From the perspective of the rule, the unexpected result is that cation valence affected flocculation at all. The fact that it did is attributed to specific adsorption (chemisorption) phenomena. Aluminum, and to a lesser degree Ca, adsorption reverses the negative charge of silicate minerals (Peng and Di 1994). Above pH 8, Ca shifts the electrophoretic mobility of Al_2O_3 to more positive values, and Ca adsorption on Al_2O_3 can be detected above pH 6 (Huang and Stumm 1973). The fact that the Ca ion was observed to suppress flocculation, although to a much smaller extent than Al, implies that limited chemisorption of Ca occurred on goethite at pH 6–6.5, increasing dispersibility. However, it should be noted that the effect of Ca relative to monovalent cations on oxide dispersibility is likely to be reversed at high pH as the oxide develops a substantial surface negative

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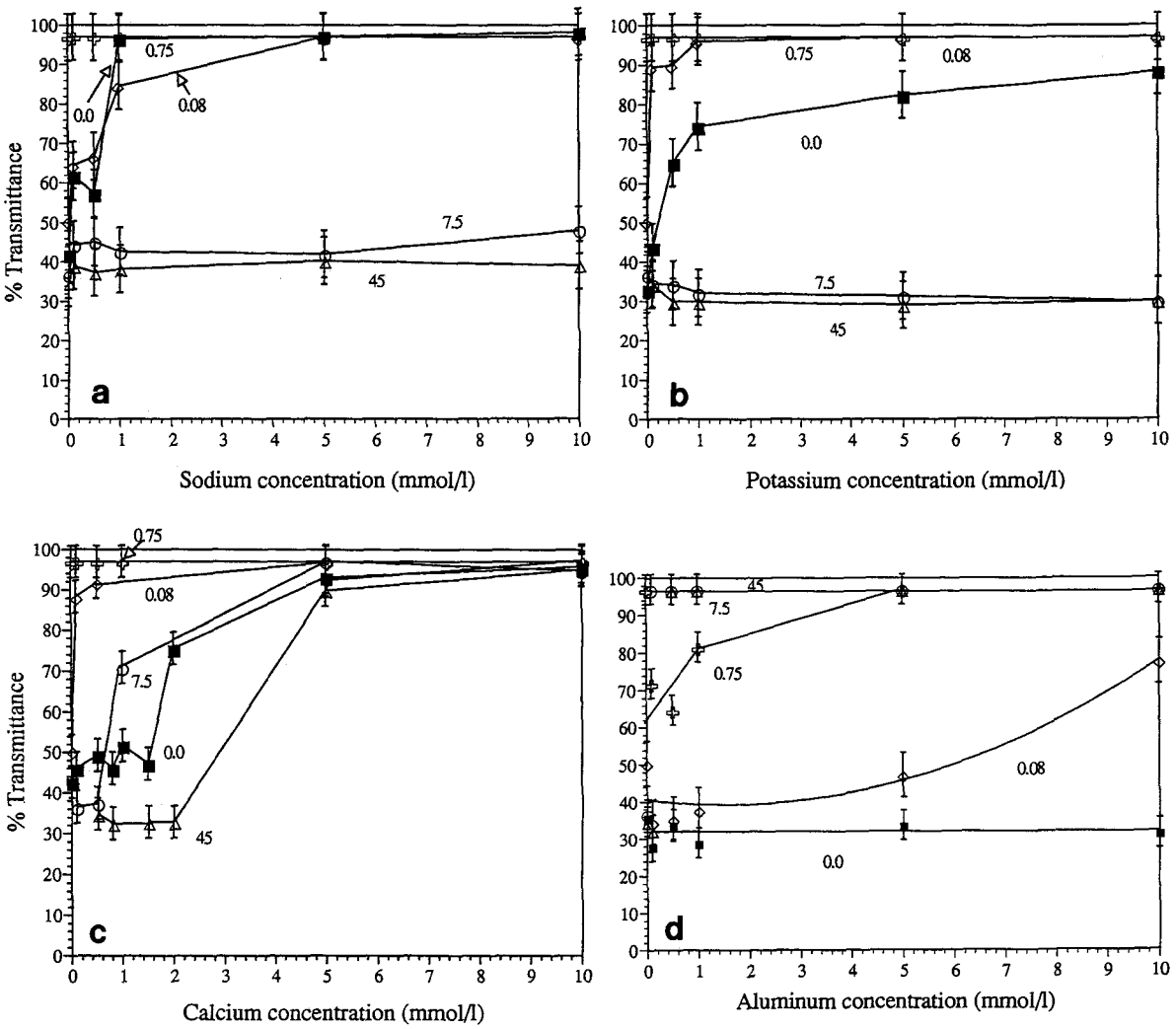


Figure 5. Transmittance of goethite suspensions at four DOC concentrations (0.08, 0.75, 7.5, 45 mg/l), measured over a range of concentrations of: a) NaCl, b) KCl, c) $CaCl_2$ and d) $AlCl_3$.

charge. Thus, in strongly alkaline media, Ca salts induce flocculation at lower concentration than Na salts (Liang and Morgan 1990). At high pH, because the counterions are cations, the Schultz-Hardy rule applies in predicting the effect of cation valence on flocculation value.

The low molecular weight organic ligands, citrate and salicylate, generally promoted flocculation, with citrate having a more pronounced effect than salicylate. However, at the higher concentrations of these ligands, there was a shift toward greater dispersibility. This trend was especially noticeable with the Ca/salicylate and K/citrate systems and least evident with the K/salicylate system, which tended to remain dispersed at low ionic strength regardless of salicylate concentration. Generally, the presence of Ca was more conducive to flocculation than K, at least when comparing the same citrate or salicylate treatments. It appears that these organic ligands interact in a complex way with the metal cations to regulate charge at the oxide surface.

The tendency of low concentrations of citrate to induce flocculation is consistent with the effect that chemisorption of citrate has in reducing the positive surface charge (Stumm 1992). Although both salicylate and citrate adsorb near pH 6–7 as inner-sphere complexes on goethite (Cornell and Schindler 1980; Yost et al. 1990; Biber and Stumm 1994), salicylate adsorbs less than citrate because it complexes less strongly with surface Fe^{3+} in this pH range (Stumm et al. 1980). This weaker interaction of salicylate with the surface could explain its less pronounced effect on flocculation. The metal cations probably modify these surface charge effects by balancing part of the ligand charge through ion pair formation. Thus, Ca^{2+} because it complexes readily with citrate, may balance excess

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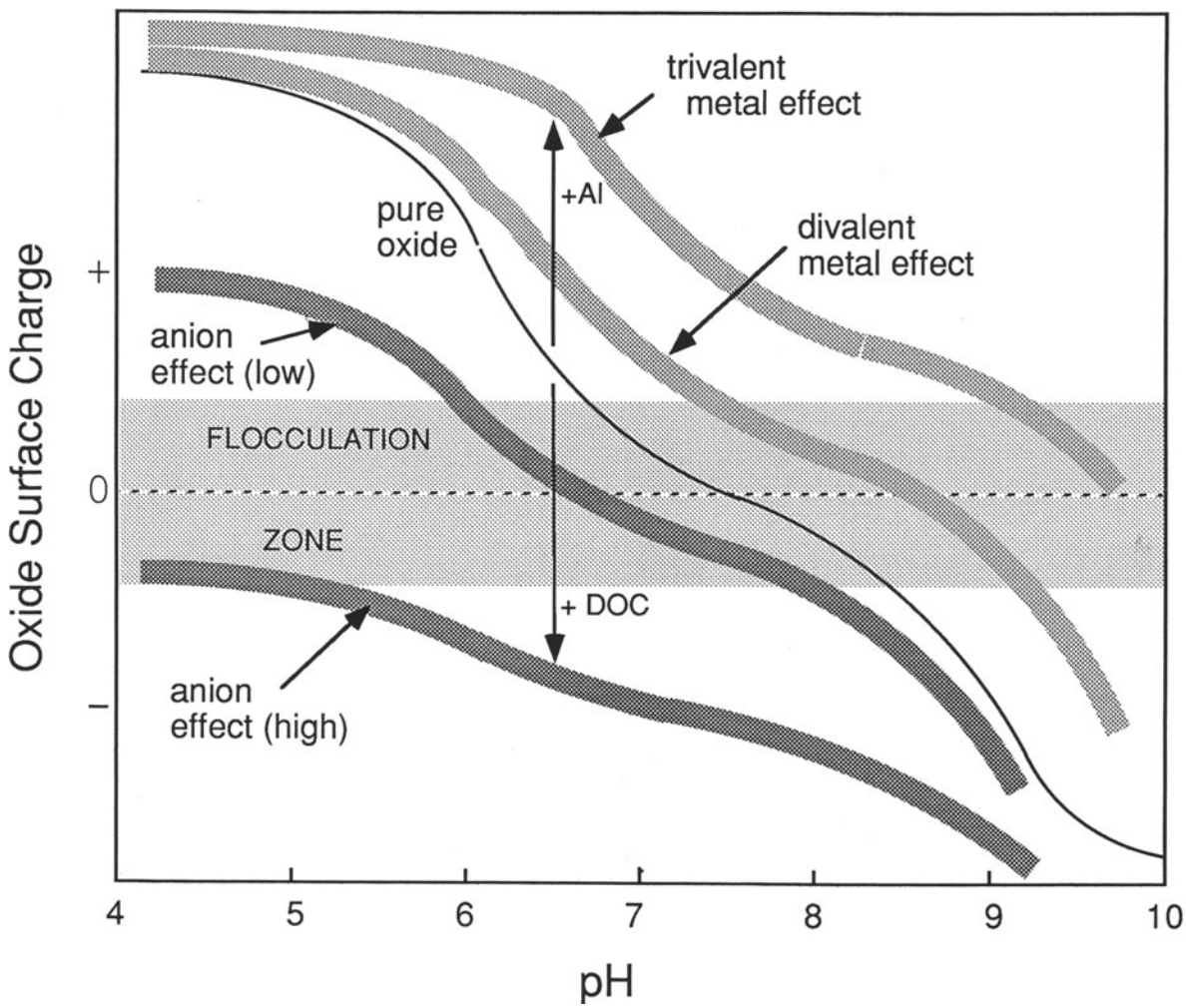


Figure 6. Depiction of the effect of divalent and trivalent metals and soluble organic ligands on oxide surface charge, with the resulting tendency for the mineral to either flocculate (shaded area) or disperse (unshaded areas).

surface negative charge resulting from citrate adsorption and prevent the Ca/citrate system from redispersing at higher citrate concentrations (Figure 2). In contrast, because inner-sphere ion pairing is not expected in the K/citrate, Ca/salicylate and K/salicylate systems, the tendency of these systems to disperse at higher ligand concentrations may be explained by a buildup of surface negative charge.

Soluble organic matter has an effect on flocculation of goethite that is qualitatively similar to that of the simple organic acids; low concentrations promote flocculation, while high concentrations induce dispersion (Figures 4 and 5). Others have noted the dispersing effects of humic substances on silicate clays and oxides in the absence of polyvalent cations (Gu and Doner 1993; Sletten and Benjamin 1994; Tipping and Higgins 1982). Liang and Morgan (1990) found that hematite and other iron oxides form relatively stable dispersions in most lake waters if the pH is near 7, ionic strength is low and the humic acid concentration exceeds 0.1 mg/l. These observations are fairly consistent with our findings regarding the stability of goethite dispersions.

Because humic substances adsorb on oxides by ligand exchange (Gu et al. 1994), adsorption tends to be favored at low pH and shifts the surface charge of the oxide from positive to negative. Thus, Davis (1982) showed that the electrophoretic mobility of a γ-Al_2O_3 suspension at pH 6.0 was strongly negative in the presence of 2.8 mg/l DOC, but nearly zero with 0.9 mg/l DOC present. This observation is consistent with our finding that 0.1–1.0 mg/l DOC induced flocculation, while >1.0 mg/l DOC promoted dispersion. The low organic level evidently favors sufficient adsorption of organic anions to neutralize surface positive charge and initiate flocculation. The higher levels reverse the charge to negative, and dispersion is again favored. The effects of DOC on dispersion are consis-

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tent with estimated anionic charge potentially added to the surfaces relative to estimated surface charge of goethite at pH 6–6.5 (calculations not shown).

The citrate and salicylate concentrations used in the experiments, which ranged from 0.01 mM to 1 mM, represent a higher concentration of ligand charge than the DOC from the organic soil, perhaps accounting for the fact that even the 0.01 mM concentration of citrate produced complete flocculation. For the natural DOC, complete flocculation tended to occur near the 0.75 mg/l DOC level, which equates to roughly 30 mmoles of ligand charge per kg of goethite, a quantity which could just balance the surface charge of goethite.

The marked dispersing effect of soluble organic matter on goethite, quite evident in the presence of Na and K salts, is partially suppressed by the presence of Ca^{2+} and completely suppressed by Al^{3+} (Figures 5c, 5d). O'Melia (1987) has reviewed the evidence for an antagonistic effect of Ca^{2+} and dissolved organic matter on the dispersion of suspended particles in natural water. The flocculating effect of Al^{3+} is not expressed at low levels of soluble organic matter, because Al^{3+} itself has a strong dispersing effect on goethite that is only overcome at higher DOC levels. Consequently, at the 0.08 and 0.75 mg/l DOC levels, the Al/goethite systems (Figure 5d) were more highly dispersed than the Na/goethite and K/goethite systems (Figures 5a, 5b).

CONCLUSIONS

Stability of goethite dispersions arises from osmotic or electrostatic repulsive forces among goethite particles, and in the absence of specifically adsorbing cations or anions, these forces are apparently reduced by higher ionic strength and flocculation is induced. As the soluble organic ligand concentration is increased, adsorption of organic anions decreases the surface positive charge and induces flocculation. Even higher concentrations of soluble organics create negative surface charge and particle dispersion results. The effect of soluble Al^{3+} and Ca^{2+}, to a smaller degree, is to attenuate or even reverse the effect of soluble organics on surface charge, thereby promoting flocculation. The overall effect of polyvalent cations and polybasic organic anions, including humic substances, on oxide mineral dispersion is accounted for by shifts in the PZC of the surface due to chemisorption. This explanation of dispersion is illustrated schematically in Figure 6, where adsorbed organic or inorganic anions shift the PZC to lower pH, and adsorbed polyvalent metals shift the PZC higher. The effect on dispersibility can be dramatic, as dissolved organic matter may shift charge sufficiently to stabilize dispersions of the oxide in the entire mid-pH range. Conversely, trivalent metals such as Al^{3+} might have little obvious effect on the dispersed state of the oxide near neutral pH, but could inhibit flocculation at alkaline pH. This diagram does not represent the importance of ionic strength in modifying these effects. For example, the dispersing effects of DOC and Ca^{2+} are suppressed at higher ionic strength.

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